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Evaluation of Analytical Methods for the Determination of POHC (Principal Organic Hazardous Constituents) in Combustion Products

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16. ABSTRACT The paper gives results of an evaluation of gas-chromatography/mass-spectrometry (GC/MS) and high-performance liquid chromatography (HPLC) methods for determining about 150 compounds from a list of potential principal organic hazardous constituents (POHCs), as defined in 40 C.F.R. Part 261, Appendix VIII. The methods evaluated are presented, analytical results are given, and the application of the evaluated methods to the determination of POHCs in incinerator effluents is discussed. These methods do not represent EPA's official method. (NOTE: As part of the Resource Conservation and Recovery Act (RCRA), the EPA has proposed regulations for owners and operators who treat hazardous waste by incineration. To ensure that these incinerators operate in an environmentally responsible manner, the regulations include a requirement that, for selected POHCs, a destruction and removal efficiency (DRE) of equal to or greater than 99.99% must be achieved (40 C.F.R. Part 264, Section 264.343). The evaluation of this paper is part of the supporting documentation for permit writers and for the incinerator-facility owners and operators.)

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ABSTRACT

EVALUATION OF ANALYTICAL METHODS FOR THE DETERMINATION OF POHC IN COMBUSTION PRODUCTS, R.H. JAMES, R.E. Adams, J.M. Finkel, H.C. Miller, Southern Research Institute, and L.D. Johnson, U.S. Environmental Protection Agency.

As part of the Resource Conservation and Recovery Act (RCRA), the U.S. Environmental Protection Agency has proposed regulations for owners and operators that treat hazardous waste by incineration. To ensure that these incinerators operate in an environmentally responsible manner, the regulations include a requirement that, for selected principal organic hazardous constituents (POHCs), a destruction and removal efficiency (DRE) of equal to or greater than 99.99% must be achieved (40 C.F.R. Part 264 § 264.343). As part of the supporting documentation for permit writers and for the incinerator-facility owners and operators, we have evaluated gas-chromatography/mass-spectrometry (GC/MS) and high-performance liquid chromatography (HPLC) methods for the determination of about 150 compounds from the list of potential POHCs, as defined in 40 C.F.R. Part 261, Appendix VIII. The methods evaluated are presented, analytical results are given, and the application of the evaluated methods to the determination of POHCs in incinerator effluents is discussed. These methods do not represent EPA's official method.

INTRODUCTION

More than 4 billion metric tons of solid waste is generated annually in the United States. Hazardous waste, produced at a rate of 30 to 40 million metric tons annually, constitutes about 1 percent of the total waste[1]. There are over 750,000 generators of hazardous wastes, 10,000 transporters, and 30,000 treatment, storage, and disposal facilities[2].

Hazardous wastes produced in the past were often disposed of improperly and unsafely. It is estimated that there are up to 50,000 uncontrolled, closed, and potentially dangerous sites in existence[1]. By the year 2000 the annual generation of hazardous waste may double. The Resource Conservation and Recovery Act[3] requires the Environmental Protection Agency to propose regulations for owners and operators who treat hazardous waste by incineration.

Monitoring proper disposal requires standard sampling and analysis procedures to determine the Principal Organic Hazardous Constituents (POHCs) in the waste and in the hazardous waste incineration effluents. As part of the supporting documentation for the permit writer and for the incinerator facility owners and operators, a manual of sampling and analytical methods has been compiled by the EPA for use in measuring the levels of POHCs in the various streams of an incinerator facility, including inlet wastes, stack gas, process waters, fly ash, and bottom ash[4]. This manual, referred to as the "Methods Manual," expands upon and augments the information in Test Methods for Evaluating Solid Waste; Physical/Chemical Methods[5], and Samplers and Sampling Procedures for Hazardous Waste Streams[6]. The Methods Manual is intended to be a resource document for permit writers and for the operators and owners of the hazardous waste incinerators.

Although the Methods Manual includes test procedures for proximate, survey, and directed (or compound-specific) analysis, the emphasis of our work was limited to directed analysis. The directed-analysis portion of the waste-characterization scheme provides confirmation of compound identity and quantitative data with appropriate quality control. These data are generated for the potentially hazardous constituents that might be expected to be present in the waste, based on engineering judgment and on the results of proximate and survey analyses.

The Methods Manual recommends a variety of directed-analysis techniques for the determination of the list of potential POHCs given in Appendix VIII, Part 261, 40 CFR. Whenever documentation was available to support the practice, the methods were written to incorporate a high-resolution analytical technique--fused-silica-capillary gas chromatography--and a highly specific detection technique--mass spectrometry. Also, whenever possible, high-performance liquid chromatography (HPLC) was recommended for the determination of compounds that could not be determined by gas chromatography with mass-spectro-

metric detection (GC/MS). Nevertheless, there were many compounds for which limited documentation was available to support the recommendation for the use of either GC/MS or HPLC. Consequently, on the basis of the demonstrated need to reduce the number and complexity of analytical methods in the Methods Manual, we developed generalized GC/MS and HPLC techniques for the determination of as many of the chemicals on the list of hazardous wastes as possible. Earlier, we reported the application of generalized analytical methods to about 70 POHCs[7]. In the effort described in the subsequent sections of this manuscript, we concentrated on approximately 80 additional POHCs.

TECHNICAL APPROACH

EXPERIMENTAL

Equipment

The GC/MS methods were developed on a Hewlett-Packard Model 5985A gas-chromatograph/mass spectrometer equipped with a HP2113 computer, a 50-megabyte HP7920M disc drive, and a magnetic tape system. The GC/flame ionization detector work was performed on a Hewlett-Packard Model 5840 gas chromatograph. Both instruments were equipped for split/splitless injections on capillary columns.

The HPLC/ultraviolet procedures were developed with the use of a Hewlett-Packard Model 1084B HPLC with a variable wavelength UV-visible detector (190-600 nm) and an automatic sampling system.

Analytical Procedures

The generalized GC/MS, GC/FID conditions are listed below:

• Instruments:	HP5985A GC/MS; HP5840 GC/FID
• Columns:	Two matched SE-54 bonded-fused-silica capillary columns, 0.32-mm ID, 25-m length
• Carrier gas:	Helium, 30 cm/s (2 mL/min)
• Injection:	2 µL splitless
• Column temperature program:	40 °C to 280 °C at 10 °/min, hold 15 min
• Injection temperature:	250 °C
• FID temperature:	250 °C
• MS parameters:	Scan 41 to 450 amu/s. Electron ionization at 70 eV. Source temperature set to 200 °C. Capillary column plumbed directly into the ion source.

These initial operating conditions were chosen as a compromise to allow the separation and detection of as many compounds as possible. Modifications of temperatures and rates may be necessary or desirable to optimize the analysis for specific compounds.

The HPLC/UV operating conditions were not confined to a single isocratic or gradient elution procedure. The instrument was a Hewlett-Packard 1084B equipped with a variable wavelength UV-VIS detector. The columns and elution options are listed below:

COLUMN: Perkin-Elmer HC-ODS-SIL-X-1, 10-µm particle size, 25-cm length x 2.6-mm ID

- Option 1A--Solvent A: Distilled, deionized water
  Solvent B: Acetonitrile
  Solvent Program: 10% B, 5 min; 10 to 100% B, 35 min; 100% B, 10 min
  Solvent Flow Rate: 1.0 mL/min
- Option 1B--Solvent A: 1% (v/v) acetic acid in distilled, deionized water
  Solvent B: Acetonitrile
  Solvent Program: 20% B, 10 min; 20 to 50% B, 10 min; 50% B, 5 min
  Solvent Flow Rate: 2 mL/min
- Option 1C--Solvent A: 1% (v/v) acetic acid in distilled, deionized water
  Solvent B: Acetonitrile
  Solvent Program: 10% B, 2 min; 10 to 100% B, 18 min
  Solvent Flow Rate: 2 mL/min
- Option 1D--Solvent A: 0.1 M acetate buffer in distilled, deionized water
  Solvent B: Acetonitrile
  Solvent Program: 10% B, 2 min; 10 to 100% B, 18 min
  Solvent Flow Rate: 1 mL/min
- Option 1E--Solvent A: 0.005 M tetrabutylammonium phosphate in distilled, deionized water
  Solvent B: Acetonitrile
  Solvent Program: 20% B, 0 min; 20 to 100% B, 20 min
  Solvent Flow Rate: 1 mL/min

COLUMN: Waters Associates µBondapak C_{18}, 10-µm particle size, 30-cm length x 3.9-mm ID

- Option 2A--Solvent A: Distilled, deionized water
  Solvent B: Acetonitrile

Solvent Program: 2% B, isocratic
Solvent Flow Rate: 1 mL/min

- Option 2B--Solvent A: Distilled, deionized water
  Solvent B: Acetonitrile
  Solvent Program: 10% B, 0 min; 10 to 100% B 30 min
  Solvent Flow Rate: 1 mL/min
- Option 2C--Solvent A: Distilled, deionized water
  Solvent B: Acetonitrile
  Solvent Program: 20% B, 20 to 100% B, 20 min; 100% B, 10 min
- Option 2D--Solvent A: 0.1 M pentane sulfonic acid in distilled, deionized water
  Solvent B: Acetonitrile
  Solvent Program: 20% B, 10 min; 20 to 80% B, 20 min
  Solvent Flow Rate: 1 mL/min

Gradient elution was required to separate most of the 49 compounds studied. The isocratic elution option (2A) was used with eight compounds. Options 1C and 2C were used in earlier work[7] but were not applied in this study and are only listed to show continuity between the two studies.

QUALITY CONTROL

We calibrated the GC/FID, GC/MS, and HPLC/UV methods with standard solutions of POHCs. For each POHC in our study, we generated five- or eight-point calibration curves. For GC/FID and GC/MS determinations, relative responses were used to give calibration curves. Relative response was calculated as a ratio of detector responses for the standard POHC to that of the internal standard, anthracene-d_{10}. We calibrated the HPLC/UV method by an external standard technique. Internal standardization of the HPLC/UV method was not used because a single internal standard that was appropriate for all HPLC/UV analyses could not be selected. In actual practice, fewer POHCs will be present in the sample and specific internal standards will be feasible. Based on the expected POHCs in a sample, the analyst will be able to select an internal standard that will not coelute with a POHC or with other organic compounds from the sample. The area response was measured at a wavelength of 254 nm and at a wavelength giving maximum absorbance or freedom from interferences. For the HPLC/UV determinations, area responses were used to give calibration curves. We then calculated a linear-regression equation and correlation coefficient from the calibration data. Typically, correlation coefficients are in excess of 0.9900. Our calibration curve can be used to estimate the sensitivity expected in the determination of a particular analyte. Also, each curve demonstrates the linearity of the detector response within the range of quantities investigated.

The precision of the determinations by GC/FID and GC/MS were assessed by triplicate injections of a standard solution of each POHC. However, for

HPLC/UV determinations, we made five replicate injections. The estimate of precision of the replicate determinations is expressed as the relative standard deviation (RSD). Typical range of RSD for GC/FID is 1% to 19%. In general, the GC/MS determinations are less precise than the GC/FID determinations. The typical range of RSD for GC/MS is 1% to 29%. The RSD for HPLC/UV determinations is less than 2%.

Any laboratory that participates in the analysis of POHCs will likely follow a formal quality-control program. The relative retention times, on-column detection limits, chromatograms, calibration curves, ion relative abundances, mass spectra, and relative standard deviations in this paper will be a guide for other analytical laboratories. Because of subtle differences among laboratories and analytical instrumentation, laboratories should generate data that will establish their own criteria for the analysis of POHCs.

Application to Environmental Samples

We applied the GC/MS screening method to four extracts from Modified Method 5 trains (MM5) from four different incineration test sites. The extracts contained 20 μg/mL of decafluorobiphenyl, naphthalene-d_8, and chrysene-d_{12} as surrogate standards. At the time of the GC/MS analysis, the samples were spiked with 20 μg/mL of anthracene-d_{10} as internal standard. The reference standard, a mixture of 156 POHCs, surrogate standards, and internal standard, was analyzed by the screening method for comparison with the incinerator samples.

RESULTS AND DISCUSSIONS

GC/FID and GC/MS Analysis

In Table I we present the retention time and on-column detection limit for each POHC we determined by GC/FID and GC/MS. The compounds are listed in the order of their elution from the GC column. Retention times are relative to that observed for the internal standard, anthracene-d_{10}. The on-column detection limit is the quantity of each analyte that was estimated to give a detector response of twice the background signal. Typical values are 0.1 to 7.0 ng for GC/FID and 0.5 to 3.5 ng for GC/MS.

The supporting documentation for our work consists of GC/FID, GC/MS, and HPLC/UV chromatograms of standard mixtures of selected POHCs. The chromatograms demonstrate the observed absolute retention times, the peak shapes, and any shifts in the baseline that occur. Also included in the documentation are the calibration curves that relate detector response to the quantity of analyte injected. Figure 1 is the GC/FID chromatogram for a standard mixture of aniline, *O,O,O*-triethylphosphorothioate, *p*-dimethylaminoazobenzene, and anthracene-d_{10} as the internal standard. The calibration curves for these three POHCs are presented in Figure 2.

In Table II we list the five most abundant mass fragments of each POHC by GC/MS. The absolute intensity of the base peak in the mass spectrum was used to develop calibration curves. The precision of replicate determinations for the GC/FID and GC/MS determinations is presented in Table III. Figure 3 shows a typical GC/MS chromatogram, and Figure 4 presents the calibration curve for the same mixture of POHCs. As part of the documentation program for POHCs submitted to GC/MS analysis, we included the mass spectrum for each POHC as demonstrated by Figure 5.

HPLC/UV Analysis

The POHCs that showed UV absorption were evaluated by one of the HPLC/UV procedures. The retention time, on-column detection limit, and wavelength of detection are given for each POHC in Table IV. The POHCs are subdivided by procedural options and then listed in the order of their elution from the HPLC column. The on-column detection limit is the quantity of each POHC that yielded a UV absorbance of about twice the background signal. Typical values are 0.5 to 25 ng. Our calibration curves were based on a detection wavelength of 254 nm. The alternate wavelength given in the table may be selected to increase sensitivity or selectivity of POHC. The precision of replicate determinations for the HPLC/UV determinations is presented in Table V.

Figure 6 is the HPLC chromatogram of a standard mixture of benzidine, 3,3-dimethylbenzidine, and 4,4'-methylene-bis(2-chloroaniline). The calibration curves for these three POHCs are presented in Figure 7.

GC/MS Analysis of Incinerator Effluent Sample Extracts

We applied the GC/MS method to the analysis of sample extracts from modified method 5 (MM5) trains from four different incineration test sites. The sample extracts are identified in Table VI. The GC/MS of a mixed POHC standard that included 156 POHCs, surrogate standards, and internal standards is given in Figure 8. We tentatively identified POHCs and other organic compounds in the extracts by their retention times and mass spectra. The major POHCs that were identified and quantified are listed in Table VII. Total-ion chromatograms of two of the extracts (I and III) are presented in Figure 9.

From these extracts we were also able to identify other organic compounds that are not POHCs. These organic compounds may come from several sources including the incinerator influent or combustion process itself. The compounds may also be artifacts due to reactions of the sorbent with materials in the incinerator effluent, the result of thermal decomposition of the residue, or the products of incomplete combustion. Because we did not analyze standards for compounds other than POHCs, we did not quantify these compounds in the sample extracts. Nevertheless, we have demonstrated the applicability of the generalized GC/MS method to samples obtained from the effluent of hazardous waste incinerators.

CONCLUSIONS

The generalized methods were standardized with organic compounds and showed acceptable precision in the determination of most of the compounds. The ultimate accuracy of the methods in the determination of POHCs in incinerator wastes and effluents will depend on the prudent choice of appropriate sampling procedures and sample-preparation procedures. We have successfully evaluated a substantial number of potential POHCs as defined in 40 C.F.R., Part 261, Appendix VIII. This data should be the foundation for the design of more comprehensive studies in support of the program for incineration of hazardous waste.

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TABLE I. SUMMARY OF GC/FID AND GC/MS DETERMINATIONS OF CANDIDATE POHCs

Compound	GC/FID		GC/MS	
	Relative retention time[a]	On-column detection limit[b], ng	Relative retention time[a]	On-column detection limit[b], ng
Methyl methacrylate	0.111	0.1	0.090	0.6
Pyridine	0.124	0.1	0.119	0.5
2-Methyllactonitrile	0.139	0.2	0.126	0.7
Ethyl methacrylate	0.146	0.1	0.125	0.4
3-Chloropropionitrile	0.168	0.1	0.160	0.3
Ethyl carbamate	0.181	1.1	0.175	5.3
Methyl methanesulfonate	0.204	0.4	0.190	0.8
Benzenethiol	0.283	0.4	0.278	0.2
Aniline	0.298	0.7	0.283	5.4
2-Chlorophenol	0.308	0.2	0.292	0.5
o-Cresol	0.371	0.2	0.356	0.6
Acetophenone	0.384	0.7	0.377	0.6
p-Cresol	0.391	0.4	0.392	0.5
m-Cresol	0.395	0.5	0.378	0.3
α,α-Dimethylphenethylamine	0.425	0.1	0.429	0.4
Dichloromethyl benzene	0.456	0.1	0.453	0.3
2,4-Dimethylphenol	0.464	0.1	0.448	0.5
O,O,O-Triethyl phosphorothioate	0.479	0.4	0.469	0.5
o-Phenylenediamine	0.523	1.0	0.527	0.6
p-Phenylenediamine	0.577	3.2	0.567	2.0
p-Chloro-m-cresol	0.596	0.4	0.585	0.9
m-Phenylenediamine	0.605	2.1	0.606	0.6
2,4,6-Trichlorophenol	0.655	1.0	0.646	1.0
Isosafrole	0.677	1.1	0.676	0.5
Dimethyl phthalate	0.747	0.5	0.738	1.1
2-Naphthylamine	0.823	1.2	0.824	0.5
2,3,4,6-Tetrachlorophenol	0.823	0.8	0.820	3.4
Diethyl phthalate	0.858	0.1	0.856	1.0
4,6-Dinitro-o-cresol	0.874	0.2	0.869	7.5
Diphenylamine	0.880	0.4	0.876	0.1
Phosphorodithioic acid ester[c]	0.936	0.3	0.932	0.5
Diallate	0.938	0.2	0.933	0.5
Dimethoate	0.964	0.6	0.961	1.1
Octamethylpyrophosphoramide	0.967	0.7	0.968	3.4
4-Aminobiphenyl	0.976	0.1	0.975	1.0
Pentachlorophenol	0.977	7.1	0.977	3.7
Pentachloronitrobenzene	0.991	0.1	0.992	3.6
Disulfoton	1.02	0.2	1.02	2.1
Methyl parathion	1.07	4.8	1.07	2.0
Di-n-butyl phthalate	1.12	0.6	1.12	0.2
Diisobutyl phthalate	1.12	0.2	1.12	6.7
Aramite	1.27	0.5	1.27	6.4
p-Dimethylaminoazobenzene	1.29	6.3	1.29	0.7
Chlorobenzilate	1.30	1.3	1.29	1.5
Kepone	1.32	0.2	1.33	5.0
Phosphorothioic acid ester[d]	1.34	3.2	1.34	1.0
Butyl benzyl phthalate	1.35	1.2	1.36	3.6
Methoxychlor	1.42	0.4	1.43	0.5
4,4'-Methylene-bis(2-chloroaniline)	1.42	1.6	1.41	3.0
Di-n-octyl phthalate	1.54	3.0	1.56	3.0
Hexachlorophene	1.63	1.1	--[e]	--[e]

[a]Relative to the retention time of anthracene-d_{10}, ≈16 min.

[b]Quantity required to yield a response twice the magnitude of the background signal.

[c]Phosphorodithioic acid, O,O-diethyl S-((ethylthio)methyl) ester.

[d]Phosphorothioic acid, O,O-dimethyl O-(p-((dimethylamino)sulfonyl)phenyl ester.

[e]Not determined by GC/MS.

TABLE II. SUMMARY OF CHARACTERISTIC EI IONS AND RELATIVE ABUNDANCES FOR CANDIDATE POHCs

Compound	mol wt	Masses of characteristic EI ions (relative abundance)				
		1	2	3	4	5
Methyl methacrylate	100	69(100)	100(58)	99(27)	41(27)	39(12)
Pyridine	79	79(100)	52(23)	78(13)	80(06)	53(02)
2-Methyllactonitrile	85	70(100)	69(06)	43(04)	71(04)	58(02)
Ethyl methacrylate	114	69(100)	99(29)	114(09)	70(05)	100(04)
3-Chloropropionitrile	89	89(100)	54(43)	91(28)	53(22)	52(09)
Ethyl carbamate	89	62(100)	44(92)	45(39)	74(34)	43(24)
Methyl methanesulfonate	110	79(100)	80(97)	95(26)	110(12)	65(12)
Benzenethiol	110	110(100)	109(26)	66(12)	111(08)	108(08)
Aniline	93	93(100)	66(26)	92(13)	65(12)	94(07)
2-Chlorophenol	128	128(100)	130(36)	64(36)	63(17)	91(14)
o-Cresol	108	108(100)	107(93)	79(22)	77(22)	90(19)
Acetophenone	120	105(100)	77(59)	120(40)	106(06)	79(06)
p-Cresol	108	107(100)	108(91)	109(07)	90(07)	91(03)
m-Cresol	108	108(100)	107(95)	79(25)	77(23)	90(11)
α,α-Dimethylphenethylamine	149	134(100)	72(19)	105(13)	135(10)	149(09)
Dichloromethylbenzene	160	125(100)	127(37)	160(17)	89(13)	162(11)
2,4-Dimethylphenol	122	122(100)	107(89)	121(50)	77(18)	91(15)
O,O,O-Triethyl phosphorothioate	198	198(100)	121(44)	97(24)	93(23)	115(21)
o-Phenylenediamine	108	108(100)	80(44)	107(24)	81(16)	53(10)
p-Phenylenediamine	108	108(100)	80(37)	107(27)	81(13)	53(09)
p-Chloro-m-cresol	142	142(100)	107(76)	144(34)	77(24)	143(14)
m-Phenylenediamine	108	108(100)	80(38)	81(23)	107(11)	53(06)
2,4,6-trichlorophenol	196	198(100)	196(96)	132(46)	97(41)	200(37)
Isosafrole	162	162(100)	131(37)	104(32)	161(29)	103(26)
Dimethyl phthalate	194	163(100)	194(15)	164(10)	77(07)	133(06)
2-Naphthylamine	143	143(100)	115(37)	116(16)	144(11)	142(06)
2,3,4,6-Tetrachlorophenol	230	232(100)	131(67)	230(67)	234(56)	55(44)
Diethyl phthalate	222	149(100)	177(24)	150(11)	176(11)	105(06)
4,6-Dinitro-o-cresol	198	198(100)	105(16)	121(11)	199(08)	168(08)
Diphenylamine	169	169(100)	168(75)	167(37)	170(15)	84(12)
Phosphorodithioic acid ester[a]	260	260(100)	75(93)	121(60)	231(46)	97(30)
Diallate	269	234(100)	236(38)	128(17)	235(15)	109(10)
Dimethoate	229	87(100)	93(51)	125(48)	143(18)	229(16)
Octamethylpyrophosphoramide	286	153(100)	135(99)	199(95)	286(74)	243(67)
4-Aminobiphenyl	169	169(100)	168(23)	170(13)	167(13)	141(08)
Pentachlorophenol	264	266(100)	264(75)	268(63)	165(38)	130(38)
Pentachloronitrobenzene	293	295(100)	237(97)	249(82)	239(73)	214(67)
Disulfoton	274	88(100)	274(96)	89(43)	153(26)	142(24)
Methyl parathion	263	109(100)	125(74)	263(42)	79(28)	93(17)
Di-n-butyl phthalate	278	149(100)	150(09)	223(08)	205(06)	104(02)
Diisobutyl phthalate	278	149(100)	150(10)	223(09)	205(06)	104(03)
Aramite	334	185(100)	319(88)	191(62)	175(59)	187(50)
p-Dimethylaminoazobenzene	225	225(100)	120(48)	226(16)	148(12)	77(11)
Chlorobenzilate	324	251(100)	253(65)	139(54)	141(19)	111(17)
Kepone	270	272(100)	274(75)	270(50)	237(50)	235(42)
Phosphorothioic acid ester[b]	325	218(100)	217(19)	93(19)	125(17)	219(10)
Butyl benzyl phthalate	312	149(100)	91(44)	206(19)	132(13)	123(12)
Methoxychlor	344	227(100)	57(65)	44(59)	55(41)	56(29)
4,4'-Methylenebis(2-chloroaniline)	266	231(100)	266(98)	268(43)	195(32)	267(30)
Di-n-octyl phthalate	390	149(100)	43(12)	44(12)	150(10)	279(09)

[a]Phosphorodithioic acid, O,O-diethyl S-((ethylthio)methyl) ester.

[b]Phosphorothioic acid, O,O-dimethyl O-(p-((dimethylamino)sulfonyl)phenyl ester.

TABLE III. PRECISION OF RESPONSE FACTORS FOR GC/FID AND GC/MS DETERMINATIONS

Compound	GC/FID		GC/MS	
	Mean[a] (n = 3)	RSD, %	Mean[a] (n = 3)	RSD, %
Acetophenone	1.04	3	0.362	18
4-Aminobiphenyl	0.671	1	0.495	15
Aniline	0.993	3	0.432	1
Aramite	0.0951	7	0.0353	10
Benzenethiol	0.221	11	0.0228	6
Butyl benzyl phthalate	0.206	11	0.401	14
Chlorobenzilate	0.302	7	0.119	13
p-Chloro-m-cresol	0.812	9	0.217	18
2-Chlorophenol	0.836	13	0.349	9
3-Chloropropionitrile	0.679	11	0.0607	24
m-Cresol	1.89	9	0.467	8
o-Cresol	1.20	14	0.259	21
p-Cresol	0.897	6	0.399	11
Diallate	0.463	11	0.207	7
Di-n-butyl phthalate	0.535	4	1.49	14
Dichloromethylbenzene	0.818	3	0.407	12
Diethyl phthalate	0.624	6	1.00	12
Diisobutyl phthalate	0.440	5	1.57	9
Dimethoate	0.160	3	0.146	9
p-Dimethylaminoazobenzene	0.270	7	0.0747	15
α,α-Dimethylphenethylamine	1.37	10	0.736	17
2,4-Dimethylphenol	0.982	2	0.234	11
Dimethyl phthalate	0.646	12	0.970	7
4,6-Dinitro-o-cresol	0.430	2	0.02257	4
Di-n-octyl phthalate	0.134	18	0.829	0
Diphenylamine	0.914	1	0.471	7
Disulfoton	0.345	1	0.0423	17
Ethyl carbamate	0.388	3	0.0961	13
Ethyl methacrylate	1.05	11	0.287	16
Hexachlorophene	0.0283	19	--[d]	--[d]
Isosafrole	0.535	6	0.228	6
Kepone	0.0392	7	0.0798	19
4,4'-Methylene-bis(2-chloroaniline)	0.104	12	--[d]	--[d]
2-Methyllactonitrile	0.555	9	0.406	11
Methyl methacrylate	1.01	12	0.190	9
Methyl methanesulfonate	0.294	4	0.132	23
Methyl parathion	0.261	6	0.254	10
Methoxychlor	0.160	4	0.327	6
2-Naphthylamine	0.897	6	0.671	1
Octamethylpyrophosphoramide	0.270	6	0.129	29
Pentachloronitrobenzene	0.287	1	0.0452	9
Pentachlorophenol	0.254	2	0.0656	6
m-Phenylenediamine	0.769	5	0.320	8
o-Phenylenediamine	0.955	1	0.351	5
p-Phenylenediamine	0.733	2	0.133	16
Phosphorodithioic acid ester[b]	0.500	1	0.453	4
Phosphorothioic acid ester[c]	0.105	11	0.169	6
Pyridine	1.40	11	0.354	28
2,3,4,6-Tetrachlorophenol	0.285	3	0.0423	7
2,4,6-Trichlorophenol	0.409	2	0.169	3
O,O,O-Triethylphosphorothioate	0.388	3	0.187	6

[a]Response Factor = $\frac{\text{Area Std}}{\text{Area IS}} \cdot \frac{\text{Conc IS}}{\text{Conc Std}}$

[b]Phosphorodithioic acid, O,O-diethyl S-((ethylthio)methyl) ester.

[c]Phosphorothioic acid, O,O-dimethyl O-(p-((dimethylamino)sulfonyl)phenyl ester.

[d]Not determined by GC/MS.

TABLE IV. SUMMARY OF HPLC/UV DETERMINATION OF CANDIDATE POHCs

Procedural option[a]	Compound	Retention time, min	On-column detection limit[b], ng (254 nm)	Optional wavelength of detection, nm	On-column detection limit[b], ng at optional wavelength
1A	Maleic anhydride[c]	1.5	6.0	210	0.4
	N-Methyl-N'-nitro-N-nitrosoguanidine	2.4	0.6	272	0.4
	Phthalic anhydride[c]	3.5	9.0	290	17.0
	4-Nitroquinoline-1-oxide	10.2	0.5	385	0.6
	3-Methylphenol	11.1	18.0	280	3.0
	4-Methylphenol	11.2	11.0	280	4.0
	2-Methylphenol	11.3	8.0	280	5.0
	Phenacetin	11.9	1.0	246	1.0
	Melphalan	13.3	1.0	260	1.0
	2,4-Dimethylphenol	15.3	15.0	280	1.0
	2,6-Dichlorophenol	15.8	10.0	280	1.0
	Benzenethiol	16.8	27.0	245	21.0
	Formaldehyde[d]	17.0	2.0	348	1.0
	2,4,5-Trichlorophenol	20.3	8.0	280	2.0
	Chloroacetaldehyde[d]	20.6	4.0	352	2.0
	Diethylstilbesterol	20.8	0.6	240	0.4
	Crotonaldehyde[d]	23.0	2.0	375	1.0
	Pentachlorophenol	23.8	12.0	280	36.0
1B	2,4-Dinitrophenol	2.8	8.0	360	23.0
	4,6-Dinitro-o-cresol	6.8	17.0	360	50.0
1D	Benzidine	8.1	0.8	268	0.2
	3,3'-Dimethoxybenzidine	9.8	2.0	298	0.9
	3,3'-Dimethylbenzidine	10.0	0.9	288	0.2
	o-Toluidine	10.0	0.9	288	0.2
	3,3'-Dichlorobenzidine	12.5	2.0	280	0.7
	4,4'-Methylenebis(2-chloroaniline)	12.7	0.6	298	2.0
1E	Trypan blue	8.2	--	588	21.0
2A	Thiourea	3.5	2.0	230	0.1
	Thiosemicarbazide	3.6	2.0	230	0.1
	Azaserine	3.6	0.2	280	0.3
	Epinephrine	4.5	1.0	280	0.1
	Thioacetamide	4.6	0.5	265	0.4
	Ethylenethiourea	4.8	4.0	242	1.0
	1-Acetyl-2-thiourea	5.6	0.8	272	0.3
	Resorcinol	8.6	3.0	280	0.7
2B	Phenylthiourea	7.2	0.7	267	0.5
	1-(o-Chlorophenyl)thiourea	9.5	1.0	262	1.0
	1-Naphthyl-2-thiourea	15.5	0.8	290	1.0
2D	Saccharin	3.4	1.0	224	0.1
	Streptozotocin	3.4	0.4	230	0.3
	Nicotine	5.1	2.0	260	2.0
	Mitomycin C	5.6	1.0	363	0.3
	Strychnine	9.5	1.0	280	3.0
	Brucine	9.6	2.0	262	0.7
	Methapyrilene	18.2	0.8	302	2.0
	Daunomycin	21.9	0.3	233	0.2
	4,4'-Methylenebis(2-chloroaniline)	24.2	0.3	298	1.0

[a]See text for description of procedural options.

[b]Estimated quantity injected that is required to yield a response twice the magnitude of the background signal at the wavelength shown.

[c]The anhydride was determined as the acid.

[d]Derivatives were made with 2,4-dinitrophenylhydrazine according to Method A131 in the Methods Manual (4).

TABLE V. PRECISION OF HPLC/UV AREA RESPONSE @254 nm

Compound	Quantity injected, µg	Area counts x 10^{-3} Mean (n = 5)	RSD, %
4-Nitroquinoline-1-oxide	1.0	585	1.4
4-Methylphenol	16.0	219	0.6
Melphalan	1.0	192	1.3
2,4-Dimethylphenol	8.0	110	0.7
2,6-Dichlorophenol	30.0	244	1.6
Formaldehyde	1.0	146	0.4
2,4,5-Trichlorophenol	5.0	53	0.5
Crotonaldehyde	1.0	127	0.5

TABLE VI. MODIFIED METHOD 5 TRAIN EXTRACTS FROM HAZARDOUS-WASTES-INCINERATION TRIAL BURN SITES

Extract	Description[a]	Surrogate Added[b]
I	XAD blank	Decafluorobiphenyl Naphthalene-d_8 Chrysene-d_{12}
II	Front XAD plus condensate	Decafluorobiphenyl Naphthalene-d_8
III	Front XAD plus condensate	Decafluorobiphenyl Naphthalene-d_8
IV	2 Front XADs plus 2 back XADs plus 2 condensates	Decafluorobiphenyl Naphthalene-d_8 Chrysene-d_{12}
V	Front XAD plus back XAD plus condensate	Decafluorobiphenyl Naphthalene-d_8 Chrysene-d_{12}

[a]Four trial burn sites are represented.

[b]Anthracene-d_{10} was added as an internal standard to GC/MS analysis.

TABLE VII. RESULTS OF ANALYSIS FOR POTENTIAL POHCs IN EXTRACTS FROM MM5 TRAIN

Tentative identification of POHCs	Concentration of POHCs in extract; ug/mL				
	I	II	III	IV	V
Benzene	--[a]	--[a]	--[a]	--[a]	
Trichloroethene		--[a]			
Trichloroethane			--[a]		
Toluene	--[a]	--[a]		--[a]	--[a]
Chlorobenzene			--[a]		
Dichloropropane		--[a]			
Dichlorobenzene			--[a]		
Bromoform			--[a]		
Chloronaphthalene			--[a]		
Hexachlorocyclopentadiene			--[a]		
Bromobenzene		2.8	99		
4-Chlorotoluene			24		
Benzaldehyde	27	98	480	1200	24
Phenol	3	8.0		300	14
2-Chlorophenol			6.9	13	
1,2,4-Trimethylbenzene	2	3.9		26	1.9
1,4-Dichlorobenzene			600	2.8	
Benzyl chloride			17		0.8
Benzyl alcohol					1.3
1,2-Dichlorobenzene			110		
N-Methylaniline			12		1.3
Acetophenone	62	56	160	1900	19
4-Methylphenol				49	
Hexachloroethane			16		
Nitrobenzene			3900		
1,2,4,5-Tetramethylbenzene		1.0		6.8	0.6
4-Chlorobenzaldehyde			330	14	
2,4-Dimethylphenol		740			5
Nitrotoluene	7	12			
Tetralin	3	3.7	11	58	2
Propiophenone	20	200	220		120
2,6-Dimethylaniline					3
Benzoic Acid	6	660	3500	250	410
2,6-Dichlorophenol			56	1.7	
1,2,4-Trichlorobenzene			220		
Naphthalene	13	13	40	170	24
4-Chlorophenol			77	330	
4-Chloroaniline			22		
Bis(2-chloroethoxy)ethane			110		
4-Chloro-3-methylphenol				17	
4-tert-Butylphenol				16	
4-Bromoaniline					
2-Methylnaphthalene		0.69	2.8	17	0.6
1,2,4,5-Tetrachlorobenzene			500		
2,4,6-Trichlorophenol			2300		
2,4,5-Trichlorophenol			120		
2-Chloronaphthalene				12	
Biphenyl				11	
1-Chloronaphthalene				10	
4-Methylquinoline			11		
2-Ethylnaphthalene		1.2		8	
Acenaphthylene					11
1,3-Dinitrobenzene			62		
Dimethyl phthalate		1.3			
2,4-Dinitrophenol			21		
Dibenzylfuran				4	
Pentachlorobenzene			4.7		
1-Aminonaphthalene			47		
Fluorene			3.4		0.9
4-Chloro-2-nitroaniline			11		
4-Nitroaniline				72	
Anthraquinone			2.9	9	
Fluoranthene		2.1			
Pyrene		1.9			
Bis(2-ethylhexyl)phthalate	3	14	71	30	16

[a]These compounds were detected but not quantified.

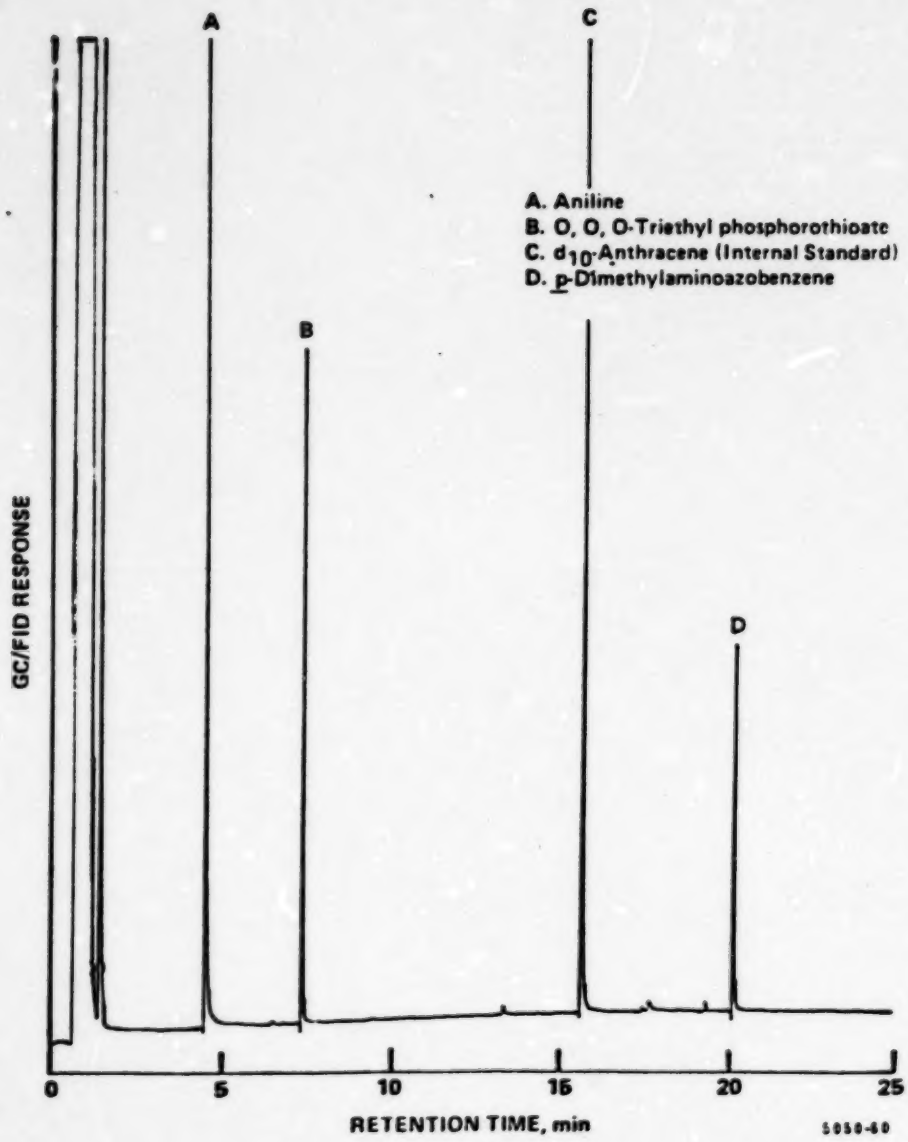

Figure 1. GC/FID chromatogram of POHC mixture.

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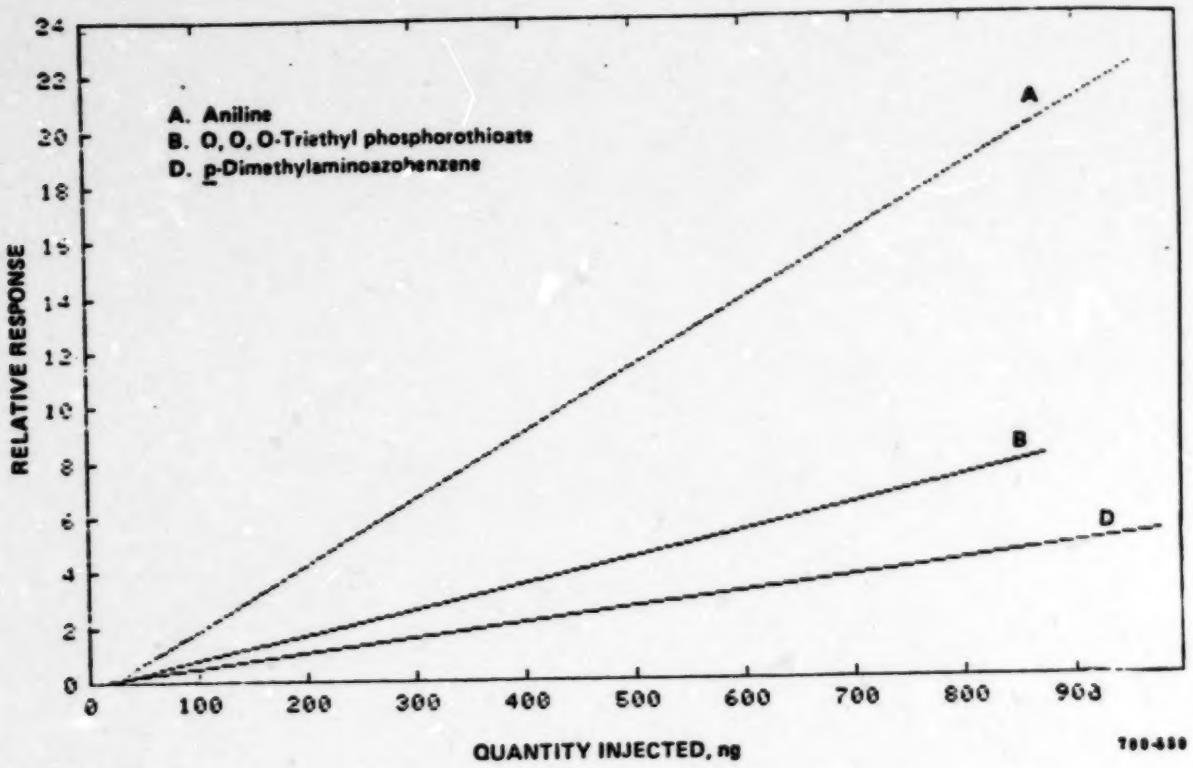

Figure 2. Calibration curves for the determination of POHCs by GC/FID.

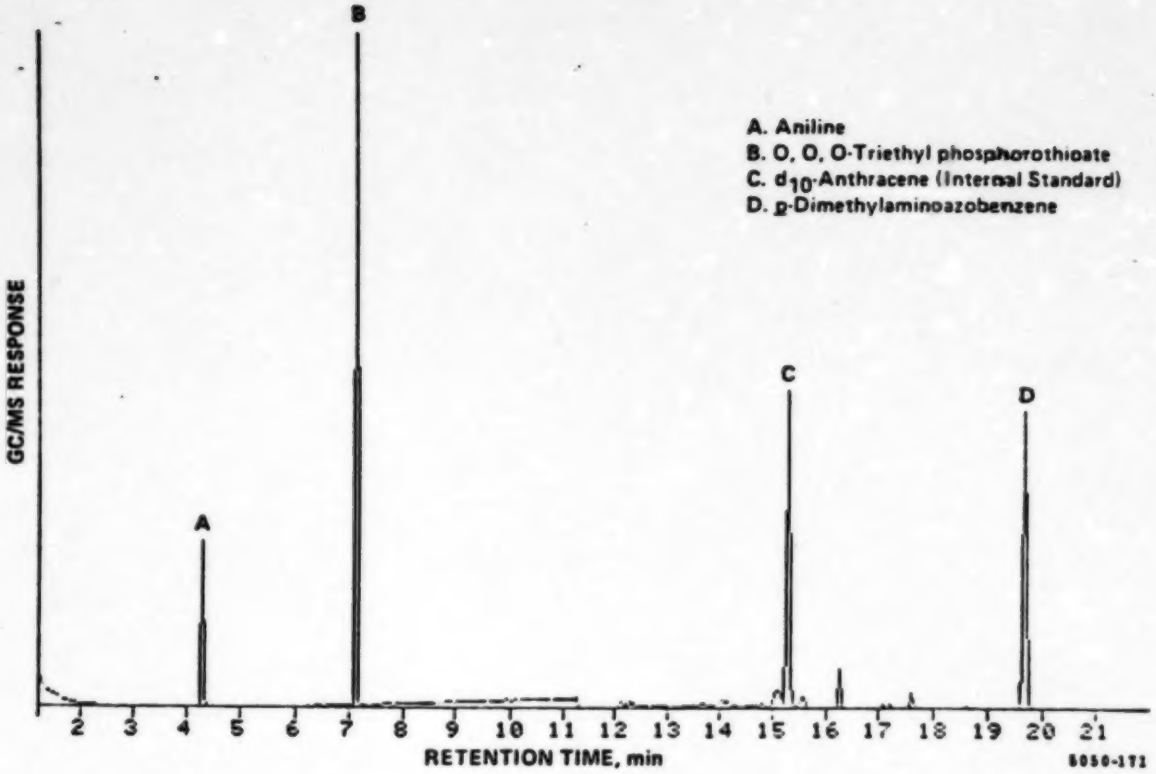

Figure 3. GC/MS chromatogram of POHC mixture.

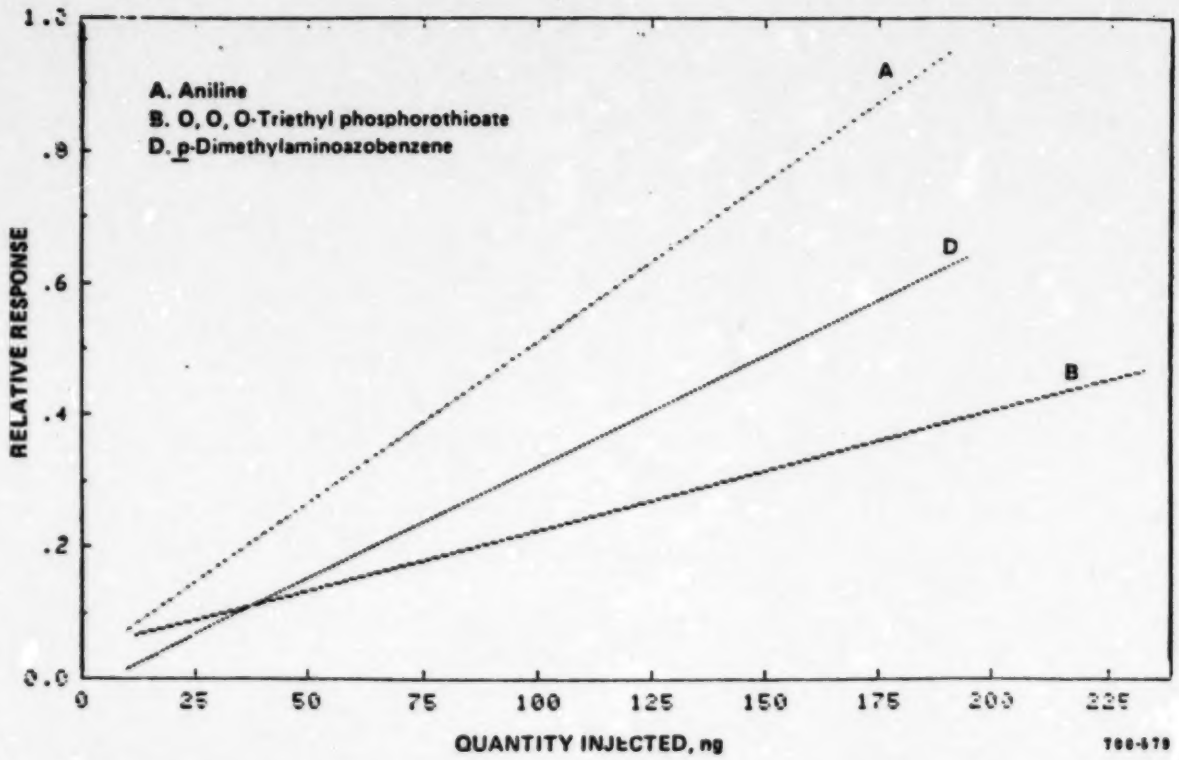

Figure 4. Calibration curves for the determination of POHCs by GC/MS.

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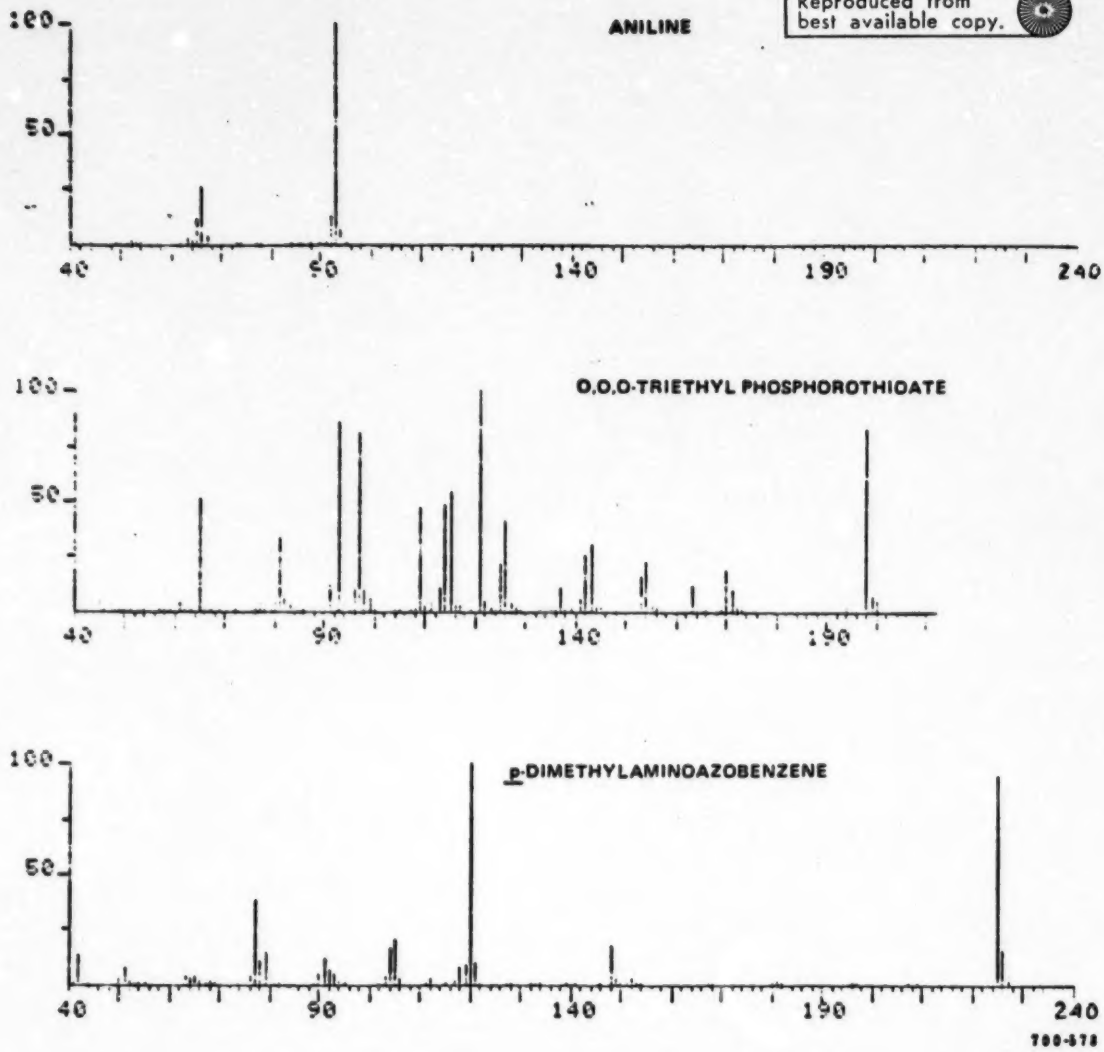

Figure 5. Mass spectra of POHCs.

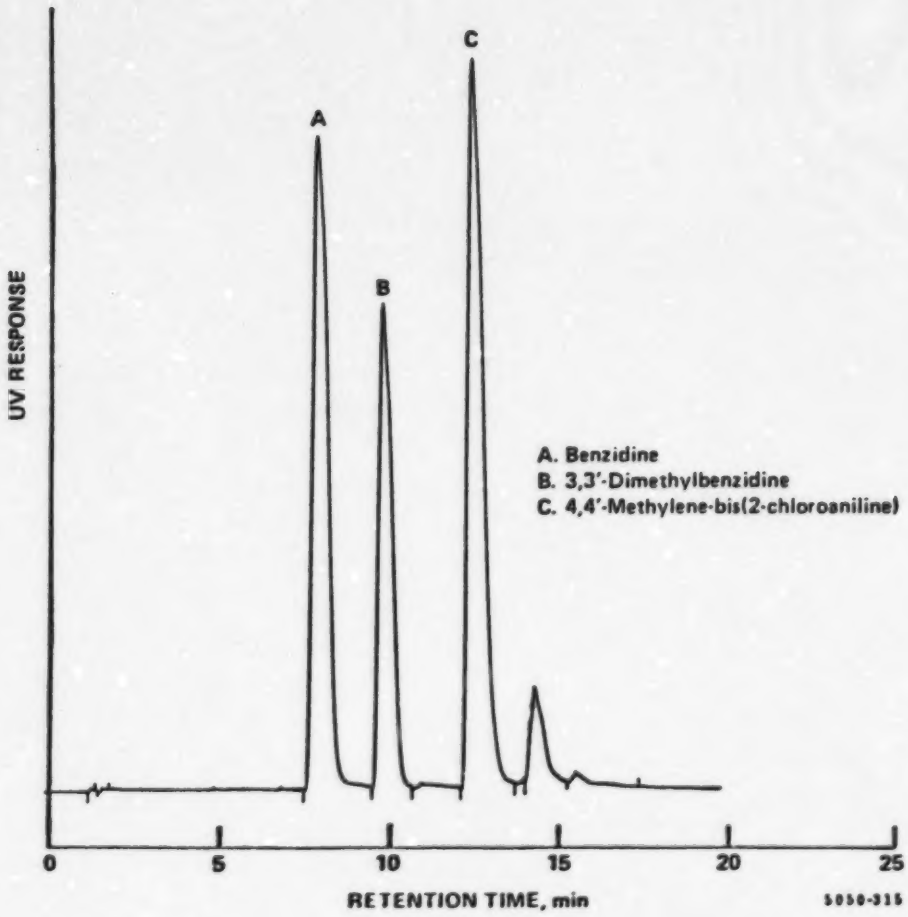

Figure 6. HPLC chromatogram (254 nm) of POHC mixture.

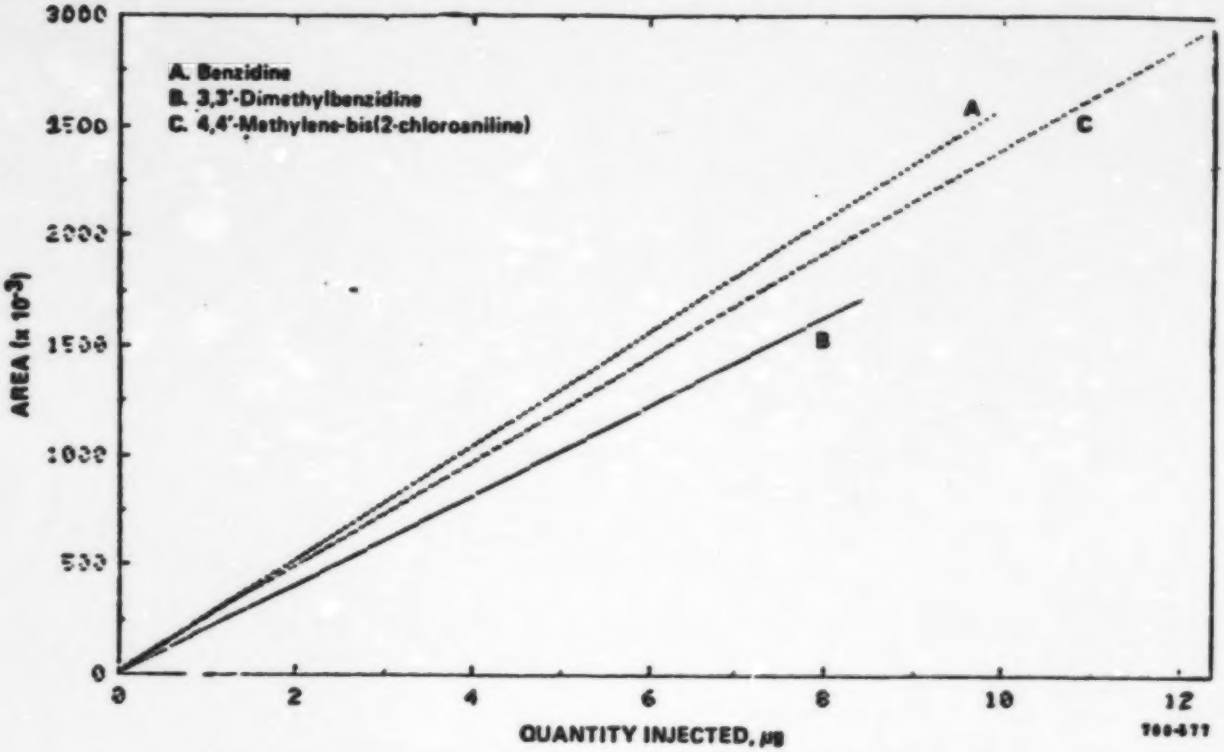

Figure 7. Calibration curve for the determination of POHCs by HPLC (254 nm).

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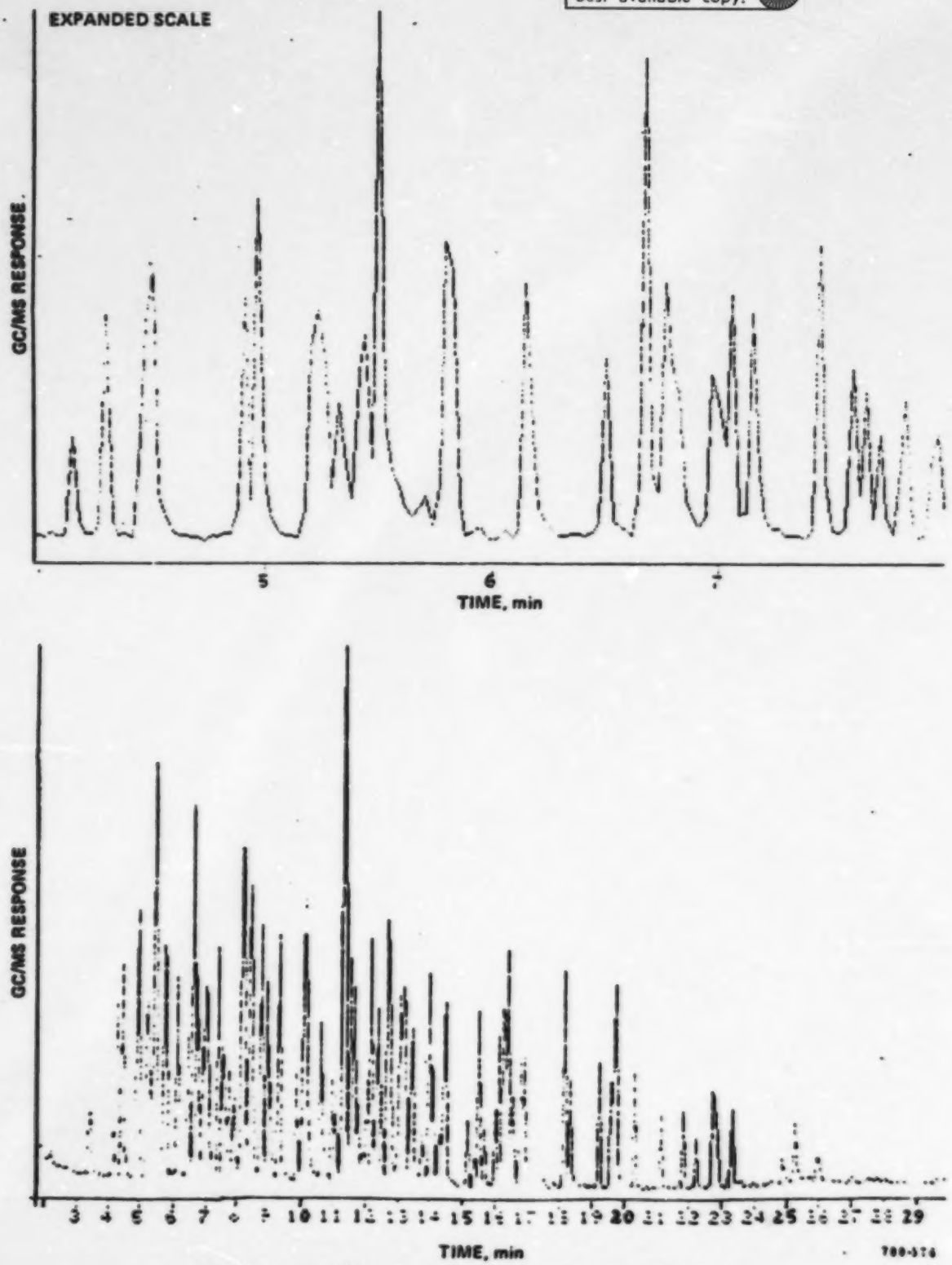

Figure 8. GC/MS chromatogram of standard POHC mixture.

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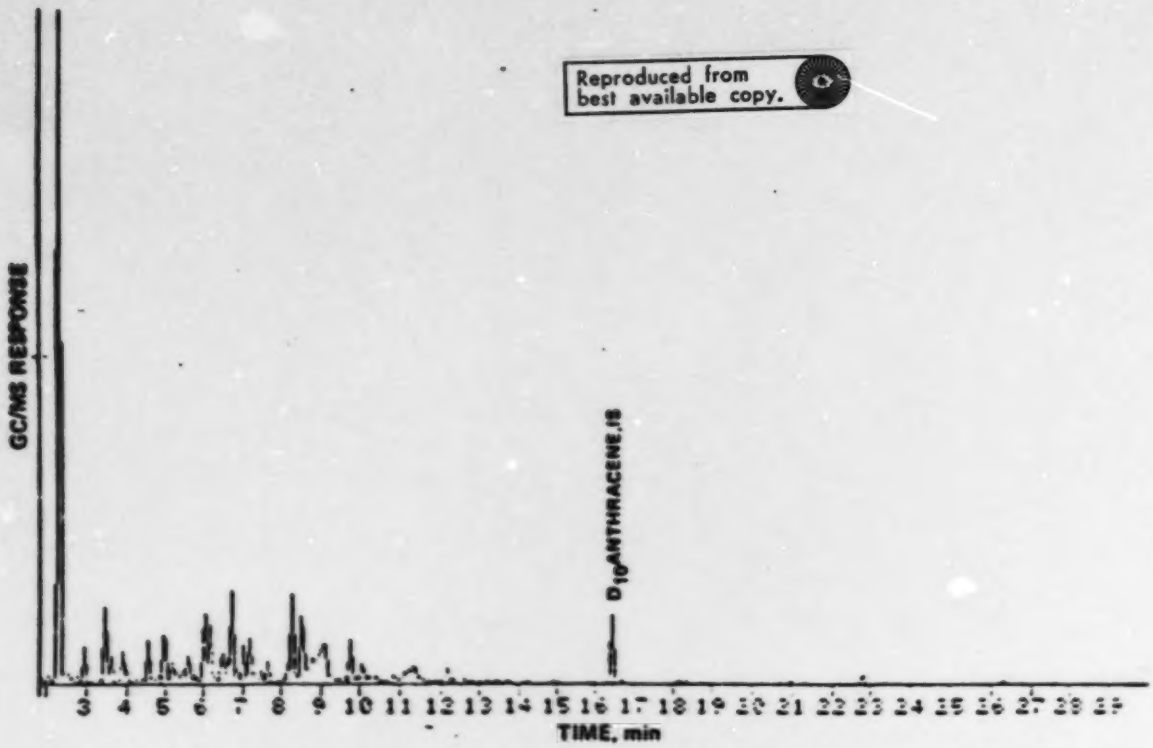

Figure 9a. GC/MS chromatogram of extract (I): XAD-2 sorbent tube, blank.

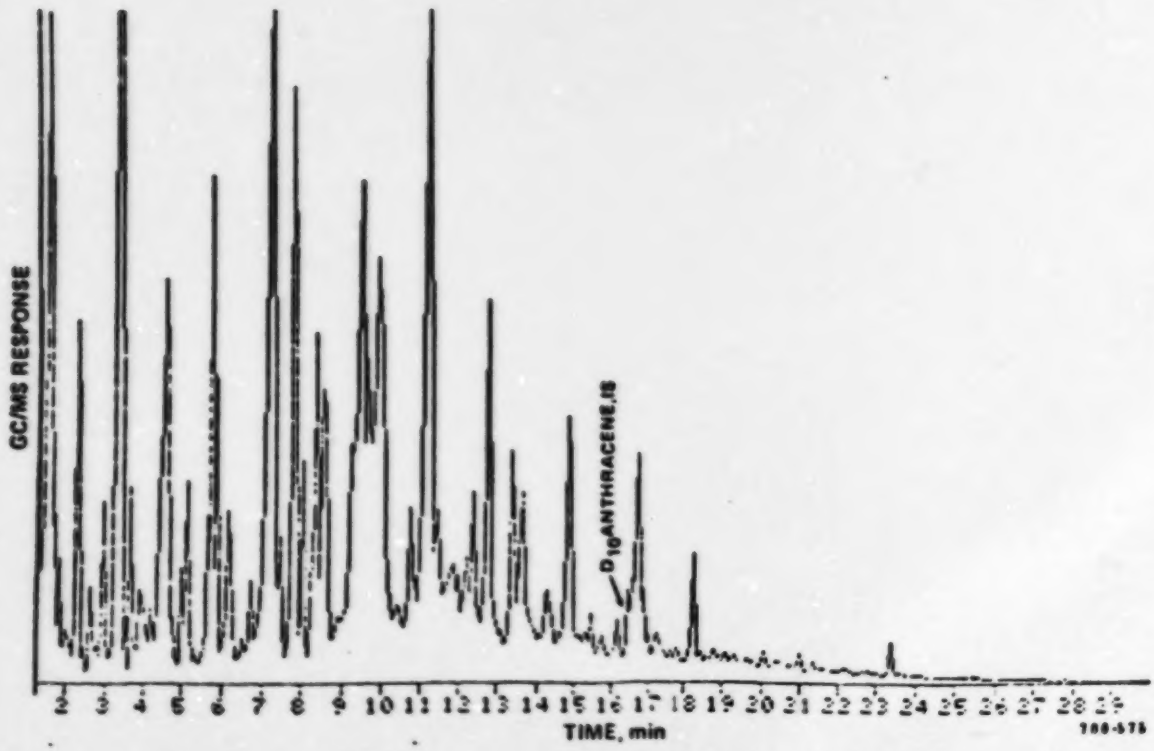

Figure 9b. GC/MS chromatogram of extract (III): XAD-2 sorbent tube, incinerator effluent.